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(54) Title: BLENDS OF α -OLEFIN/VINYLDENE AROMATIC MONOMER AND/OR HINDERED ALIPHATIC OR CYCLOALIPHATIC VINYLDENE MONOMER INTERPOLYMERS

(57) Abstract

Blends of polymeric materials comprising a plurality of interpolymers each having (1) from 0.5 to 65 mole percent of either (a) at least one vinylidene aromatic monomer or (b) at least one hindered aliphatic or cycloaliphatic vinylidene monomer, or (c) a combination of at least one vinylidene aromatic monomer and at least one hindered aliphatic vinylidene monomer, and (2) from 35 to 99 mole percent of at least one aliphatic alpha olefin having from 2 to 20 carbon atoms; and wherein interpolymer components differ in that (i) the amount of vinylidene aromatic monomer residue and/or hindered aliphatic or cycloaliphatic vinylidene monomer residue in any interpolymer component differs from another by at least 0.5 mole percent; and/or (ii) there is a difference of at least 20 percent between the number average molecular weight (M_n) of interpolymer components. These blends of interpolymer components give enhanced properties or processability when compared to the individual polymers comprising the blend.

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BLEND OF α -OLEFIN/VINYLDENE AROMATIC MONOMER AND/OR HINDERED
ALIPHATIC OR CYCLOALIPHATIC VINYLDENE MONOMER INTERPOLYMERS

The present invention pertains to blends of α -olefin/vinyldene aromatic monomer and/or hindered aliphatic or cycloaliphatic vinyldene monomer interpolymers having different vinyldene aromatic monomer and/or hindered aliphatic or cycloaliphatic vinyldene monomer content or different molecular weight or both different vinyldene aromatic monomer and/or hindered aliphatic or cycloaliphatic vinyldene monomer content and different molecular weight. The blend components are selected to provide superior performance or processability in the blends.

The generic class of materials covered by α -olefin/hindered vinyldene monomer substantially random interpolymers and including materials such as α -olefin/vinyl aromatic monomer interpolymers are known in the art and offer a range of material structures and properties which makes them useful for varied applications, such as compatibilizers for blends of polyethylene and polystyrene as described in US 5,460,818.

One particular aspect described by D'Anniello et al. (Journal of Applied Polymer Science, Volume 58, pages 1701-1706 [1995]) is that such interpolymers can show good elastic properties and energy dissipation characteristics. In another aspect, selected interpolymers can find utility in adhesive systems, as illustrated in United States patent number 5,244,996, issued to Mitsui Petrochemical Industries Ltd.

Although of utility in their own right, Industry is constantly seeking to improve the applicability of these interpolymers. Such enhancements may be accomplished via additives or the like, but it is desirable to develop technologies to provide improvements in processability and/or performance without the addition of additives or further improvements than can be achieved with the addition of additives. To date, the possible advantages of blending to provide materials with superior properties have not been identified.

There is a need to provide blends of α -olefin/vinyldene aromatic monomer interpolymers with superior performance characteristics which will expand the utility of this interesting class of materials.

The present invention pertains to a blend of polymeric materials characterized by a plurality of interpolymers, each interpolymer resulting from polymerizing:

- (1) from 1 to 65 mole percent of
(a) at least one vinylidene aromatic monomer, or
(b) at least one hindered aliphatic or cycloaliphatic vinylidene monomer, or
5 (c) a combination of at least one vinylidene aromatic monomer and at least one hindered aliphatic or cycloaliphatic vinylidene monomer, and
(2) from 35 to 99 mole percent of at least one aliphatic α -olefin having from 2 to 20 carbon atoms; and
10 (3) from 0 to 10 mole percent of at least one polymerizable olefin monomer different from (2); and
wherein each of the interpolymer blend components are distinct in that:
15 (i) the amount of vinylidene aromatic monomer residue and/or hindered aliphatic or cycloaliphatic vinylidene monomer residue in any interpolymer differs from that amount in any other interpolymer by at least 0.5 mole percent; and/or
(ii) there is a difference of at least 20 percent between the number average molecular weight (M_n) in any interpolymer and any other 20 interpolymer.

The blends of the present invention can comprise, consist essentially of or consist of any two or more of such interpolymers enumerated herein. Likewise, the interpolymers can comprise, consist essentially of or consist of any two or more of the enumerated 25 polymerizable monomers.

These blends provide an improvement in one or more of the polymer properties such as mechanical performance and/or melt processability.

The percent difference in comonomer content (vinylidene aromatic 30 monomer residue and/or hindered aliphatic or cycloaliphatic vinylidene monomer residue) between the interpolymers in the blends of the present invention is determined by subtracting the comonomer content of the interpolymer with the lowest comonomer content from the interpolymer with the highest comonomer content. In those instances 35 where more than 2 interpolymers are employed in the blend, the percent difference is determined for each combination of two polymers for example for a blend of interpolymers A, B and C, the determination is made for the combinations: A & B, A & C and B & C.

The percent difference in M_n between the interpolymers in the 40 blends of the present invention is determined by subtracting the M_n of the interpolymer with the lowest M_n from the interpolymer with the highest M_n and dividing the difference with the M_n of the interpolymer

with the lowest Mn, then multiplying by 100. In those instances where more than 2 interpolymers are employed in the blend, the percent difference is determined for each combination of two polymers for example for a blend of interpolymers A, B and C, the determination is made for the combinations: A & B, A & C and B & C.

The term "hydrocarbyl" means any aliphatic, cycloaliphatic, aromatic, aryl substituted aliphatic, aryl substituted cycloaliphatic, aliphatic substituted aromatic, or cycloaliphatic substituted aromatic groups. The aliphatic or cycloaliphatic groups are preferably saturated. Likewise, the term "hydrocarbyloxy" means a hydrocarbyl group having an oxygen linkage between it and the carbon atom to which it is attached.

The term "plurality" as used herein means two or more.

The term "interpolymer" is used herein to indicate a polymer wherein at least two different monomers are polymerized to make the interpolymer. This includes copolymers, terpolymers, etc

The term "substantially random" in the substantially random interpolymer resulting from polymerizing one or more α -olefin monomers and one or more vinylidene aromatic monomers or hindered aliphatic or cycloaliphatic vinylidene monomers, and optionally, with other polymerizable ethylenically unsaturated monomer(s) as used herein means that the distribution of the monomers of said interpolymer can be described by the Bernoulli statistical model or by a first or second order Markovian statistical model, as described by J. C.

Randall in POLYMER SEQUENCE DETERMINATION, Carbon-13 NMR Method, Academic Press New York, 1977, pp. 71-78. Preferably, the substantially random interpolymer resulting from polymerizing one or more α -olefin monomers and one or more vinylidene aromatic monomers, and optionally, with other polymerizable ethylenically unsaturated monomer(s) does not contain more than 15 percent of the total amount of vinylidene aromatic monomer residue in blocks of vinylidene aromatic monomer of more than 3 units. More preferably, the interpolymer is not characterized by a high degree of either isotacticity or syndiotacticity. This means that in the carbon-¹³ NMR spectrum of the substantially random interpolymer the peak areas corresponding to the main chain methylene and methine carbons representing either meso diad sequences or racemic diad sequences should not exceed 75 percent of the total peak area of the main chain methylene and methine carbons.

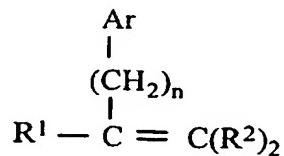
Any numerical values recited herein include all values from the lower value to the upper value in increments of one unit provided that there is a separation of at least 2 units between any lower value and

any higher value. As an example, if it is stated that the amount of a component or a value of a process variable such as, for example, temperature, pressure, time is, for example, from 1 to 90, preferably from 20 to 80, more preferably from 30 to 70, it is intended that values such as 15 to 85, 22 to 68, 43 to 51, 30 to 32 etc. are expressly enumerated in this specification. For values which are less than one, one unit is considered to be 0.0001, 0.001, 0.01 or 0.1 as appropriate. These are only examples of what is specifically intended and all possible combinations of numerical values between the lowest value and the highest value enumerated are to be considered to be expressly stated in this application in a similar manner.

The interpolymers employed in the present invention include, but are not limited to, substantially random interpolymers prepared by polymerizing one or more α -olefin monomers with one or more vinylidene aromatic monomers and/or one or more hindered aliphatic or cycloaliphatic vinylidene monomers, and optionally with other polymerizable ethylenically unsaturated monomer(s).

Suitable α -olefin monomers include for example, α -olefin monomers containing from 2 to 20, preferably from 2 to 12, more preferably from 2 to 8 carbon atoms. Preferred such monomers include ethylene, propylene, butene-1, 4-methyl-1-pentene, hexene-1 and octene-1. Most preferred are ethylene or a combination of ethylene with C₂₋₈ α -olefins. These α -olefins do not contain an aromatic moiety.

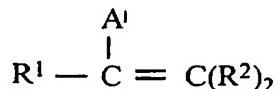
Suitable vinylidene aromatic monomers which can be employed to prepare the interpolymers employed in the blends include, for example, those represented by the following formula:



wherein R¹ is selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms, preferably hydrogen or methyl; each R² is independently selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms, preferably hydrogen or methyl; Ar is a phenyl group or a phenyl group substituted with from 1 to 5 substituents selected from the group consisting of halo, C₁₋₄-alkyl, and C₁₋₄-haloalkyl; and n has a value from zero to 4, preferably from zero to 2, most preferably zero. Exemplary monovinylidene aromatic monomers include styrene, vinyl toluene, α -methylstyrene, t-butyl

styrene, chlorostyrene, including all isomers of these compounds. Particularly suitable such monomers include styrene and lower alkyl- or halogen-substituted derivatives thereof. Preferred monomers include styrene, α -methyl styrene, the lower alkyl- ($C_1 - C_4$) or 5 phenyl-ring substituted derivatives of styrene, such as for example, ortho-, meta-, and para-methylstyrene, the ring halogenated styrenes, para-vinyl toluene or mixtures thereof. A more preferred aromatic monovinylidene monomer is styrene.

By the term "hindered aliphatic or cycloaliphatic vinylidene 10 compounds", it is meant addition polymerizable vinylidene monomers corresponding to the formula:



wherein A^1 is a sterically bulky, aliphatic or cycloaliphatic substituent of up to 20 carbons, R^1 is selected from the group of 15 radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms, preferably hydrogen or methyl; each R^2 is independently selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms, preferably hydrogen or methyl; or alternatively R^1 and A^1 together form 20 a ring system. By the term "sterically bulky" is meant that the monomer bearing this substituent is normally incapable of addition polymerization by standard Ziegler-Natta polymerization catalysts at a rate comparable with ethylene polymerizations. α -Olefin monomers containing from 2 to 20 carbon atoms and having a linear aliphatic 25 structure such as propylene, butene-1, hexene-1 and octene-1 are not considered as hindered aliphatic monomers. Preferred hindered aliphatic or cycloaliphatic vinylidene compounds are monomers in which one of the carbon atoms bearing ethylenic unsaturation is tertiary or 30 quaternary substituted. Examples of such substituents include cyclic aliphatic groups such as cyclohexyl, cyclohexenyl, cyclooctenyl, or ring alkyl or aryl substituted derivatives thereof, tert-butyl, norbornyl. Most preferred hindered aliphatic or cycloaliphatic vinylidene compounds are the various isomeric vinyl- ring substituted 35 derivatives of cyclohexene and substituted cyclohexenes, and 5- ethylidene-2-norbornene. Especially suitable are 1-, 3-, and 4- vinylcyclohexene.

Other optional polymerizable ethylenically unsaturated monomer(s) include strained ring olefins such as norbornene and C_{1-10}

alkyl or C₆₋₁₀ aryl substituted norbornenes, with an exemplary interpolymer being ethylene/styrene/norbornene.

The number average molecular weight (Mn) of the polymers and interpolymers is usually greater than 5,000, preferably from 20,000 to 5 1,000,000, more preferably from 50,000 to 500,000.

Polymerizations and unreacted monomer removal at temperatures above the autopolymerization temperature of the respective monomers may result in formation of some amounts of homopolymer polymerization products resulting from free radical polymerization. For example, 10 while preparing the substantially random interpolymer, an amount of atactic vinylidene aromatic homopolymer may be formed due to homopolymerization of the vinylidene aromatic monomer at elevated temperatures. The presence of vinylidene aromatic homopolymer is in general not detrimental for the purposes of the present invention and 15 can be tolerated. The vinylidene aromatic homopolymer may be separated from the interpolymer, if desired, by extraction techniques such as selective precipitation from solution with a non solvent for either the interpolymer or the vinylidene aromatic homopolymer. For the purpose of the present invention it is preferred that no more than 20 20 weight percent, preferably less than 15 weight percent based on the total weight of the interpolymers of vinylidene aromatic homopolymer is present.

The substantially random interpolymers may be modified by typical grafting, hydrogenation, functionalizing, or other reactions 25 well known to those skilled in the art. The polymers may be readily sulfonated or chlorinated to provide functionalized derivatives according to established techniques.

The substantially random interpolymers can be prepared as described in US Application Number 07/545,403 filed July 3, 1990 30 (corresponding to EP-A-0,416,815) by James C. Stevens et al. and in allowed US Application Number 08/469,828 filed June 6, 1995 all of which are incorporated herein by reference in their entirety. Preferred operating conditions for such polymerization reactions are pressures from atmospheric up to 3,000 atmospheres and temperatures 35 from -30°C to 200°C.

Examples of suitable catalysts and methods for preparing the substantially random interpolymers are disclosed in U.S. Application No. 07/545,403, filed July 3, 1990 corresponding to EP-A-416,815; U.S. Application No. 07/702,475, filed May 20, 1991 corresponding to EP-A-40 514,828; U.S. Application No. 07/876,268, filed May 1, 1992 corresponding to EP-A-520,732; U.S. Application No. 08/241,523, filed May 12, 1994; as well as U.S. Patents: 5,055,438; 5,057,475; 5,096,867;

5,064,802; 5,132,380; 5,189,192; 5,321,106; 5,347,024; 5,350,723; 5,374,696; 5,399,635; 5,460,993 and 5,556,928 all of which patents and applications are incorporated herein by reference in their entirety.

The substantially random α -olefin/vinylidene aromatic interpolymers can also be prepared by the methods described by John G. Bradfute et al. (W. R. Grace & Co.) in WO 95/32095; by R. B. Pannell (Exxon Chemical Patents, Inc.) in WO 94/00500; and in Plastics Technology, p. 25 (September 1992), all of which are incorporated herein by reference in their entirety.

Also suitable are the substantially random interpolymers which comprise at least one α -olefin/vinyl aromatic/vinyl aromatic/ α -olefin tetrad disclosed in U. S. Application No. 08/708,809 filed September 4, 1996 by Francis J. Timmers et al. These interpolymers contain additional signals with intensities greater than three times the peak to peak noise. These signals appear in the chemical shift range 43.75-44.25 ppm and 38.0-38.5 ppm. Specifically, major peaks are observed at 44.1, 43.9 and 38.2 ppm. A proton test NMR experiment indicates that the signals in the chemical shift region 43.75-44.25 ppm are methine carbons and the signals in the region 38.0-38.5 ppm are methylene carbons.

In order to determine the carbon¹³ NMR chemical shifts of the interpolymers described, the following procedures and conditions are employed. A five to ten weight percent polymer solution is prepared in a mixture consisting of 50 volume percent 1,1,2,2-tetrachloroethane-d₂ and 50 volume percent 0.10 molar chromium tris(acetylacetone) in 1,2,4-trichlorobenzene. NMR spectra are acquired at 130°C using an inverse gated decoupling sequence, a 90° pulse width and a pulse delay of five seconds or more. The spectra are referenced to the isolated methylene signal of the polymer assigned at 30.000 ppm.

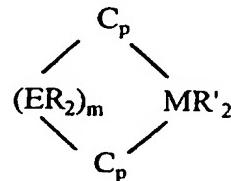
It is believed that these new signals are due to sequences involving two head-to-tail vinyl aromatic monomer preceded and followed by at least one α -olefin insertion, for example an ethylene/styrene/styrene/ethylene tetrad wherein the styrene monomer insertions of said tetrads occur exclusively in a 1,2 (head to tail) manner. It is understood by one skilled in the art that for such tetrads involving a vinyl aromatic monomer other than styrene and an α -olefin other than ethylene that the ethylene/vinyl aromatic monomer/vinyl aromatic monomer/ethylene tetrad will give rise to similar carbon¹³ NMR peaks but with slightly different chemical shifts.

The interpolymers which contain hindered cycloaliphatic monomer residues are usually prepared by subjecting an interpolymer containing monovinylidene aromatic monomer residues to hydrogenation therefore converting some or all of the aromatic rings to cycloaliphatic rings which can be saturated (for example, cyclohexane ring) or unsaturated (cyclohexene ring).

The interpolymers of one or more α -olefins and one or more monovinylidene aromatic monomers and/or one or more hindered aliphatic or cycloaliphatic vinylidene monomers employed in the present invention are substantially random polymers.

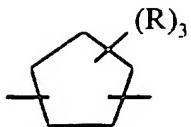
These interpolymers usually contain from 0.5 to 65, preferably from 1 to 55, more preferably from 2 to 50 mole percent of at least one vinylidene aromatic monomer and/or hindered aliphatic or cycloaliphatic vinylidene monomer and from 35 to 99.5, preferably from 45 to 99, more preferably from 50 to 98 mole percent of at least one aliphatic α -olefin having from 2 to 20 carbon atoms.

These interpolymers are prepared by conducting the polymerization at temperatures of from -30°C to 250°C in the presence of such catalysts as those represented by the formula



20

wherein: each C_p is independently, each occurrence, a substituted cyclopentadienyl group π -bound to M; E is C or Si; M is a group IV metal, preferably Zr or Hf, most preferably Zr; each R is independently, each occurrence, H, hydrocarbyl, silahydrocarbyl, or hydrocarbysilyl, containing up to 30 preferably from 1 to 20 more preferably from 1 to 10 carbon or silicon atoms; each R' is independently, each occurrence, H, halo, hydrocarbyl, hydrocarbyloxy, silahydrocarbyl, hydrocarbysilyl containing up to 30 preferably from 1 to 20 more preferably from 1 to 10 carbon or silicon atoms or two R' groups together can be a C_{1-10} hydrocarbyl substituted 1,3-butadiene; m is 1 or 2; and optionally, but preferably in the presence of an activating cocatalyst. Particularly, suitable substituted cyclopentadienyl groups include those illustrated by the formula:



wherein each R is independently, each occurrence, H, hydrocarbyl, silahydrocarbyl, or hydrocarbysilyl, containing up to 30 preferably from 1 to 20 more preferably from 1 to 10 carbon or silicon atoms or 5 two R groups together form a divalent derivative of such group. Preferably, R independently each occurrence is (including where appropriate all isomers) hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, benzyl, phenyl or silyl or (where appropriate) two such R groups are linked together forming a fused ring system such as 10 indenyl, fluorenyl, tetrahydroindenyl, tetrahydrofluorenyl, or octahydrofluorenyl.

Particularly preferred catalysts include, for example, racemic-(dimethylsilanediyl(2-methyl-4-phenylindenyl))zirconium dichloride, racemic-(dimethylsilanediyl(2-methyl-4-phenylindenyl))zirconium 1,4-diphenyl-1,3-butadiene, racemic-(dimethylsilanediyl(2-methyl-4-phenylindenyl))zirconium di-C₁₋₄ alkyl, racemic-(dimethylsilanediyl(2-methyl-4-phenylindenyl))zirconium di-C₁₋₄ alkoxide, or any combination thereof.

Further preparative methods for the interpolymer components of 20 the present invention have been described in the literature. Longo and Grassi (Makromol. Chem., Volume 191, pages 2387 to 2396 [1990]) and D'Anniello et al. (Journal of Applied Polymer Science, Volume 58, pages 1701-1706 [1995]) reported the use of a catalytic system based on methylalumoxane (MAO) and cyclopentadienyltitanium trichloride 25 (CpTiCl₃) to prepare an ethylene-styrene copolymer. Xu and Lin (Polymer Preprints, Am.Chem.Soc., Div.Polym.Chem.) Volume 35, pages 686, 687 [1994]) have reported copolymerization using a MgCl₂/TiCl₄/NdCl₃/Al(iBu)₃ catalyst to give random copolymers of styrene and propylene. Lu et al (Journal of Applied Polymer Science, 30 Volume 53, pages 1453 to 1460 [1994]) have described the copolymerization of ethylene and styrene using a TiCl₄/NdCl₃/MgCl₂/Al(Et)₃ catalyst. Sernetz and Mulhaupt, (Macromol. Chem. Phys., v. 197, pp 1071-1083, 1997) have described the influence of 35 polymerization conditions on the copolymerization of styrene with ethylene using Me₂Si(Me₂Cp)(N-tert-butyl)TiCl₂/methylaluminoxane Ziegler-Natta catalysts. The manufacture of α -olefin/vinyl aromatic monomer interpolymers such as propylene/styrene and butene/styrene are described in United States patent number 5,244,996, issued to Mitsui Petrochemical Industries Ltd.

The present invention provides blends of interpolymer components of molecular weight and composition distributions selected to obtain an overall molecular weight and composition distribution which gives enhanced properties or processability.

- 5 The interpolymer blend components are distinct in that:
- (i) the amount of vinylidene aromatic monomer residue and/or hindered aliphatic or cycloaliphatic vinylidene monomer residue in any interpolymer component differs from another by at least 0.5 mole percent, preferably by at least 1 mole percent and most preferably by 10 2 mole percent; and/or
 - (ii) there is a difference of at least 20 percent, preferably at least 30 percent and most preferably at least 40 percent between the number average molecular weight (M_n) of interpolymer components.

In one embodiment, the components for the blend are 15 interpolymers having a relatively narrow molecular weight distribution, with $M_w/M_n < 3.5$. Utilizing these interpolymers as components, the invention provides interpolymers having plural modality with respect to comonomer residue content and a narrow molecular weight distribution, such that $M_w/M_n < 3.5$.

20 In another aspect, the invention provides interpolymers having plural modality with respect to molecular weight, such that $M_w/M_n > 3.5$ and produced from component interpolymers having essentially the same comonomer residue contents.

In still another aspect, the invention provides interpolymers 25 having plurality with respect to both molecular weight distribution, such that $M_w/M_n > 3.5$, and produced from component polymers having a difference in comonomer content.

A further aspect of the present invention pertains to blends comprising two or more substantially random interpolymers of styrene 30 and ethylene or styrene and a combination of ethylene and one or more other polymerizable monomers, wherein the substantially random interpolymer components have a difference in styrene content of from 2 to less than 10 wt. percent. These blends can be considered as miscible, in that such blends exhibit a single glass transition 35 temperature (T_g) similar in form to, but in the temperature range between the T_g 's of the individual polymers. These blend compositions are particularly suitable, for example, to optimize processability.

Another aspect of the present invention pertains to blends comprising two or more substantially random interpolymers of styrene 40 and ethylene or styrene and a combination of ethylene and one or more other polymerizable monomers, wherein the substantially random interpolymer components have a difference in styrene content of

greater than 10 wt.%. These blend compositions can be considered as immiscible blends, in that they exhibit a broadened single glass transition temperature range, or exhibit two or more glass transition temperatures which reflects the behavior of the individual polymers.

5 These blends are particularly suitable for applications including those which require energy absorption over specific temperature ranges, such as sound and vibration damping.

Also contemplated are blend compositions comprising three or more components wherein two or more components show miscible behavior

10 using Tg criteria, but the overall blend composition exhibits a broadened single glass transition temperature range, or exhibits two or more distinct glass transition temperatures.

The blends of the present invention may be prepared by any suitable means known in the art such as, but not limited to, dry

15 blending in a pelletized form in the desired proportions followed by melt blending in a screw extruder, Banbury mixer or the like. The dry blended pellets may be directly melt processed into a final solid state article by for example injection molding. Alternatively, the

20 blends may be made by direct polymerization, without isolation of the blend components, using for example two or more catalysts in one reactor, or by using a single catalyst and two or more reactors in series or parallel.

Additives such as antioxidants (for example, hindered phenols such as, for example, IRGANOX® 1010), phosphites (for example,

25 IRGAFOS® 168)), U. V. stabilizers, cling additives (for example, polyisobutylene), antiblock additives, slip agents, colorants, pigments, fillers can also be included in the interpolymers employed in the blends of the present invention, to the extent that they do not interfere with the enhanced properties discovered by Applicants.

30 The additives are employed in functionally equivalent amounts known to those skilled in the art. For example, the amount of antioxidant employed is that amount which prevents the polymer or polymer blend from undergoing oxidation at the temperatures and environment employed during storage and ultimate use of the polymers.

35 Such amounts of antioxidants is usually in the range of from 0.01 to 10, preferably from 0.05 to 5, more preferably from 0.1 to 2 percent by weight based upon the weight of the polymer or polymer blend.

Similarly, the amounts of any of the other enumerated additives are the functionally equivalent amounts such as the amount to render

40 the polymer or polymer blend antiblocking, to produce the desired amount of filler loading to produce the desired result, to provide the desired color from the colorant or pigment. Such additives can

suitably be employed in the range of from 0.05 to 50, preferably from 0.1 to 35 more preferably from 0.2 to 20 percent by weight based upon the weight of the polymer or polymer blend. However, in the instance of fillers, they could be employed in amounts up to 90 percent by 5 weight based on the weight of the polymer or polymer blend.

The blends of the present invention can be utilized to produce, but not limited to, a wide range of fabricated articles such as, for example, calendered sheet, blown or cast films, injection molded, rotomolded or thermoformed parts. The blends can also be used in the 10 manufacture of fibers, foams and latices. The blends of the present invention can also be utilized in adhesive formulations.

The following examples are illustrative of the invention, but are not to be construed as to limiting the scope thereof in any manner.

15 **EXAMPLES**

Preparation of Interpolymers A, B, C, and E

Polymer was prepared in a 400 gallon agitated semi-continuous batch reactor. The reaction mixture consisted of approximately 250 gallons of a solvent comprising a mixture of cyclohexane (85 weight 20 percent) and isopentane (15 weight percent), and styrene. Prior to addition, solvent, styrene and ethylene were purified to remove water and oxygen. The inhibitor in the styrene was also removed. Inerts were removed by purging the vessel with ethylene. The vessel was then pressure controlled to a set point with ethylene. Hydrogen was added 25 to control molecular weight. Temperature in the vessel was controlled to set-point by varying the jacket water temperature on the vessel. Prior to polymerization, the vessel was heated to the desired run temperature and the catalyst components: Titanium: (N-1,1-dimethylethyl)dimethyl(1-(1,2,3,4,5-eta)-2,3,4,5-tetramethyl- 2,4- 30 cyclopentadien-1-yl)silanaminato)) (2-N)-dimethyl, CAS# 135072-62-7, Tris(pentafluorophenyl)boron, CAS# 001109-15-5, Modified methylalumin-oxane Type 3A, CAS# 146905-79-5, were flow controlled, on a mole ratio basis of 1/3/5 respectively, combined and added to the vessel. After starting, the polymerization was allowed to proceed with ethylene 35 supplied to the reactor as required to maintain vessel pressure. In some cases, hydrogen was added to the headspace of the reactor to maintain a mole ratio with respect to the ethylene concentration. At the end of the run, the catalyst flow was stopped, ethylene was removed from the reactor, 1000 ppm of Irganox™ 1010 anti-oxidant was 40 then added to the solution and the polymer was isolated from the solution. Catalyst efficiency was generally greater than 100,000 # polymer per # Ti. The resulting polymers were isolated from solution

by either stripping with steam in a vessel or by use of a devolatilizing extruder. In the case of the steam stripped material, additional processing was required in extruder-like equipment to reduce residual moisture and any unreacted styrene.

Inter-polymer	Solvent loaded		Styrene loaded		Pressure		Temp. ° C	Total H ₂ Added Grams	Run Time Hours	Polymer in Solution Wt. %
	lbs	kg	lbs	kg	Psi g	kPa				
(A)	252	114	1320	599	42	290	60	0	2.8	11.5
(B)	839	381	6610	300	105	724	60	53.1	4.8	11.6
(C)	1196	542	2252	102	70	483	60	7.5	6.1	7.2
(E)	842	382	6620	300	105	724	60	8.8	3.7	8.6

5

Interpolymer	Melt Index I ₂	Total Wt% Styrene Residue in Polymer*	Talc Level Wt %	Isolation Method
(A)	0.18	81.7	<2.5	Steam Strip
(B)	2.6	45.5	0	Extruder
(C)	0.03	29.8	0	Extruder
(E)	0.01	48.3	<1.0	Steam Strip

* Total wt. percent styrene residue measured via Fourier Transform Infrared (FTIR) technique.

Preparation of Interpolymer D

10 Interpolymer D was prepared in the following manner. A 130 mL continuous loop reactor, consisting of two static mixers, a gear pump (1200 mL/min), inlets for liquids and gasses, a viscometer and a pair of thermocouples, was used to prepare the polymer. The reactor temperature was maintained by external heating 15 tapes. Pressure was monitored at the liquid inlet and controlled via a variable valve on the outlet. The reactor was fed with a mixture of 75 weight percent styrene and 25 weight percent toluene at 12.00 mL/min, ethylene at 0.700 g/min, hydrogen at 0.411 mg/min and a catalyst system composed of 0.001 M toluene solutions of tert-butylamidodimethyl(tetramethylcyclopenta-dienyl)silanetitanium-dimethyl and tris-(pentafluoro-phenyl)borane both at 0.25 mL/min. The reactor temperature was held at 100°C and the viscosity allowed to stabilize at ~15 cP (0.015 Pa·s). The resulting polymer solution was blended with 0.05 mL/min of a catalyst deactivator/polymer stabilizer 20 solution (1 L of toluene, 20 g of Irganox 1010 and 15 mL of 2- 25 solution (1 L of toluene, 20 g of Irganox 1010 and 15 mL of 2-

Propanol), cooled to ambient temperature and collected for 20 hours and 50 minutes. The solution was dried in a vacuum oven overnight, resulting in 750g of a 16.6 mole percent styrene residue ethylene/styrene copolymer with 6.5 weight percent atactic polystyrene 5 having a melt index greater than 200.

Test parts and characterization data for the interpolymers and their blends were generated according to the following procedures:

Compression Molding: Samples were melted at 190°C for 3 minutes and compression molded at 190°C under 20,000 lb (9,072 kg) of pressure 10 for another 2 minutes. Subsequently, the molten materials were quenched in a press equilibrated at room temperature.

Density: The density of the samples is measured according to ASTM-D792.

Differential Scanning Calorimetry (DSC): A Dupont DSC-2920 is 15 used to measure the thermal transition temperatures and heat of transition for the interpolymers. In order to eliminate previous thermal history, samples were first heated to 200 °C. Heating and cooling curves were recorded at 10°C/min. Melting (from second heat) and crystallization temperatures were recorded from the peak 20 temperatures of the endotherm and exotherm, respectively.

Melt Shear Rheology: Oscillatory shear rheology measurements were performed with a Rheometrics RMS-800 rheometer. Rheological properties were monitored at an isothermal set temperature of 190°C in a frequency sweep mode.

Solid state dynamic mechanical testing: Dynamic mechanical properties of compression molded samples were monitored using a Rheometrics 800E mechanical spectrometer. Samples were run in torsion 25 rectangular geometry and purged under nitrogen to prevent thermal degradation. Typically, samples were run at a fixed forced frequency of 10 rad/sec using a torsional set strain of 0.05%, and collecting data isothermally at 4°C intervals.

Mechanical Testing: All properties were generated at 23°C. Shore A hardness is measured following ASTM-D240. Flexural modulus is evaluated according to ASTM-D790. Tensile properties of the 35 compression molded samples were measured using an Instron 1145 tensile machine equipped with an extensiometer. ASTM-D638 samples were tested at a strain rate of 5 min⁻¹. The average of four tensile measurements is given. The yield stress and yield strain were recorded at the inflection point in the stress/strain curve. The Energy at break is 40 the area under the stress/strain curve.

Tensile Stress Relaxation: Uniaxial tensile stress relaxation is evaluated using an Instron 1145 tensile machine. Compression

molded film (~ 20 mil thick) with a 1 in. (25.4 mm) gauge length is deformed to a strain level of 50 percent at a strain rate of 20 min⁻¹. The force required to maintain 50 percent elongation is monitored for 10 min. The magnitude of the stress relaxation is defined as (f_i - f_f/f_i) where f_i is the initial force and f_f is the final force.

The characteristics of each of the interpolymers were given in table 1. The unblended interpolymers provide the comparative examples employed herein.

Table 1

Interpolymer Composition	INTERPOLYMER				
	(A)	(B)	(C)	(D)	(E)
wt % atactic Polystyrene ^c	8.6	10.3	1	6.5	3.7
wt % Styrene Residue ^c	69.4	43.4	29.3	42.4	47.3
wt % Ethylene Residue ^c	30.6	56.6	70.7	57.6	52.7
mol % Styrene Residue ^c	37.9	17.1	10	16.5	19.5
mol % Ethylene Residue ^c	62.1	82.9	90	83.5	80.5
Molecular Weight					
MFR, I ₂	0.18	2.62	0.03	> 200	0.01
$M_n \times 10^3$	161.1	66.8	118.1	13.6	144.9
M_w/M_n (polydispersity)	2.11	1.89	2.04	13.1	2.26
Physical Properties					
Density, g/cc	1.0352	0.9626	0.943	0.9756	0.9604
T _m , °C	a	49.6	71.3	62.1	45.7
% Crystallinity	a	4.8	14.7	4.6	4.7
T _c , °C	a	22.1	58.1	46.6	17
T _g (DSC)	24.2	-12	-17.2	a	-12.7
Mechanical Properties					
Shore A	96	75	88	78	76
Tensile Modulus, Mpa	594.3	6.5	20	19.3	6.8
Flexural Modulus, Mpa	617.1	68.8	62.1	84.8	140.7
Yield Stress, MPa	5.6	1.3	2.4	2.3	1.5
% Strain @ Break	257.8	475.3	377.5	412.8	337.8
Stress @ Break, Mpa	21.5	22.6	34.3	2.5	17.4
Energy @ Break, N·m	118.5	102.2	145.5	33.9	73.2
% Stress Relaxation	92.9	38	30.2	43.2	26.2
Melt Rheology					
$\eta \times 10^5$ (0.1 rad/sec), Poise	6.53	1.05	16.6	b	31
η (100/0.1)	0.048	0.15	0.16	b	0.038
Tan δ (0.1 rad/sec)	4.42	4.2	2.37	b	1.26

a Could not be measured by DSC.

b Could not be measured.

c Measured by N.M.R. techniques

EXAMPLES 1-3

Blend Preparation: Three blend compositions, examples 1, 2 and 3, were prepared from interpolymers (A) and (B) above in weight ratios of (A)/(B) of 75/25, 50/50 and 25/75 with a Hakke mixer equipped with a Rheomix 3000 bowl. The blend components were first dry blended and then fed into the mixer equilibrated at 190°C. Feeding and

temperature equilibration took 3 to 5 minutes. The molten material is mixed at 190°C and 40 rpm for 10 minutes.

The characterization data for the blends and the interpolymer components was presented in table 2. Interpolymer blend components 5 (A) and (B) have molecular weights which were significantly different, and styrene content which differ by 28 mol. percent.

Table 2

	Example or Comparative Experiment No.				
	(A)*	(B)*	1	2	3
Blend Composition, wt ratio	100% (A)	100% (B)	(A) / (B) 75/25	(A) / (B) 50/50	(A) / (B) 25/75
styrene residue mole % difference	N/A*	N/A*	20.8	20.8	20.8
% Mn difference	N/A*	N/A*	141	141	141
Mechanical Properties					
Shore A	96	75	96	91	80
Tensile Modulus, MPa	594.3	6.5	1143.2	326.8	28.2
Flexural Modulus, MPa	617.1	68.8	531.1	169.9	24.4
Yield Stress, MPa	5.6	1.3	10.8	4.6	2.3
% Strain @ Break	257.8	475.3	287.7	370.2	415.6
Stress @ Break, MPa	21.5	22.6	23.7	25	25.5
Energy @ Break, N·m	118.5	102.2	146.3	152.4	126.8
% Stress Relaxation	92.9	38	86.9	82.2	67.2
Melt Rheology					
$\eta \times 10^{-5}$ (0.1 rad/sec), Poise	6.53	1.05	3.75	2.34	1.57
η (100/0.1)	0.048	0.15	0.058	0.078	0.16
Tan δ (0.1 rad/sec)	4.42	4.2	2.16	2.46	2.14

* Not an example of the present invention

a Not applicable

10 Table 2 shows that the blend composition examples 1, 2 and 3 all have high tensile energies at break, which significantly exceed the performance of the unblended interpolymers, comparative examples (A) and (B). Further, the blends retain an unexpected level of stress 15 relaxation compared to what may be anticipated from the component polymers.

Blend examples 1, 2 and 3 also have tan δ values at low shear rates in the melt which were significantly lower than either of the component polymers (A) and (B). This translates to higher melt 20 elasticity and improved part forming characteristics under certain melt processing operations.

EXAMPLE 4

A blend composition, example 4, was prepared from interpolymers (A) and (C) in a 50/50 weight ratio of components, according to the 25 same procedure employed in examples 1-3.

The characterisation data for the blends and the interpolymer components was presented in table 3. Interpolymer blend components (A) and (C) have molecular weights (M_n) which both exceed 100,000 and styrene residue contents which differ by 28 mol. percent.

5

Table 3

	Example or Comparative Experiment No.		
	(A)*	(C)*	4
Blend Composition, wt ratio	100% (A)	100% (C)	(A)/(C) 50/50
styrene residue mole % difference	N/A*	N/A*	27.9
% Mn difference	N/A*	N/A*	36.4
Mechanical Properties			
Shore A	96	88	96
Tensile Modulus, MPa	594.3	20	424.7
Flexural Modulus, MPa	617.1	62.1	202
Yield Stress, MPa	5.6	2.4	5.9
% Strain @ Break	257.8	377.5	313
Stress @ Break, MPa	21.5	34.3	37
Energy @ Break, N·m	118.5	145.5	188
% Stress Relaxation	92.9	30.2	75.1
Melt Rheology			
$\eta \times 10^{-5}$ (0.1 rad/sec), Poise	6.53	16.6	10.3
η (100/0.1)	0.048	0.16	0.048
Tan δ (0.1 rad/sec)	4.42	2.37	2.14

* Not an example of the present invention
a Not applicable

Table 3 shows the blend composition example 4 has a high tensile energy at break, which significantly exceeds the performance of the unblended interpolymers, comparative examples (A) and (C). Further, the blend retains a level of stress relaxation biased towards the performance of component (A).

Blend example 4 also has a tan δ value at low shear rates in the melt which was lower than either of the component polymers (A) and (C). The shear thinning [η (100/0.1)] of the blend, related to melt processing characteristics, was identical to that of component (A).

EXAMPLES 5-8

Interpolymer blend component (D) has a significantly lower number average molecular weight (M_n) and broader molecular weight distribution (higher M_w/M_n) compared to the other four interpolymers, (A), (B), (C) and (E). Interpolymer blend component (D) has a different styrene content to interpolymers (A) and (C), and an essentially similar styrene residue content to interpolymer (E), differing by only 3 mol. percent.

Blends were prepared from interpolymer (D) and interpolymers (A), (C) and (E) in a 10/90 weight ratio of components to give examples 5, 6 and 7 respectively, and from interpolymers (D) and (C) in a 30/70 weight ratio of components to give example 8, according to
5 the same procedure employed in examples 1-3.

The characterization data for the blend examples and the interpolymer components was presented in table 4.

Table 4 shows that blend component interpolymer, and comparative example, (D) was a low viscosity polymer with low tensile energy to
10 break.

Table 4

	Example or Comparative Experiment No.							
	(A)*	(C)*	(D)*	(E)*	5	6	7	8
Blend Composition, wt ratio	100% (A)	100% (C)	100% (D)	100% (E)	(D)/(A) 10/90	(D)/(E) 10/90	(D)/(C) 10/90	(D)/(C) 30/70
styrene residue mole% difference	N/A ^c	N/A ^c	N/A ^c	N/A ^c	21.4	3	6.5	6.5
% Mn difference	N/A ^c	N/A ^c	N/A ^c	N/A ^c	1,126	965	768	768
Mechanical Properties								
Shore A	96	88	78	76	95	73	84	82
Tensile Modulus, MPa	594.3	20	19.3	6.8	550.9	8.3	24.8	20.7
Flexural Modulus, MPa	617.1	62.1	84.8	140.7	96.5	28.3	64.1	51
Yield Stress, MPa	5.6	2.4	2.3	1.5	4.8	1.3	2.4	2.2
% Strain @ Break	257.8	377.5	412.8	337.8	260.6	475.8	372.3	452.4
Stress @ Break, MPa	21.5	34.3	2.5	17.4	24.9	22.7	25	28.4
Tensile Energy @ Break, N·m	118.5	145.5	33.9	73.2	125.2	118	126	150.4
% Stress Relaxation	92.9	30.2	43.2	26.2	90.9	33.4	30.1	32.8
Melt Rheology								
$\eta \times 10^{-5}$ (0.1 rad/sec)	6.53	16.6	b	31	4.25	12	4.15	5.3
η (100/0.1)	0.048	0.16	b	0.038 ^a	0.052	0.066	0.043	0.046
Tan δ (0.1 rad/sec)	4.42	2.37	b	1.26	4.44	2.33	2.61	3.74

* Not an example of the present invention

a $\eta(100/3.98)$

b Could not be measured

c Not applicable

15

Blend examples 5, 6, 7 and 8 all show that even low additions of (D) brings very large reductions in viscosity [$\eta \times 10^{-5}$ (0.1 rad/sec)] for interpolymers (A), (C) and (E). This was achieved whilst retaining or
20 enhancing the mechanical properties of interpolymers (A), (C) and (E), as was clearly shown by the tensile energy to break data, and stress relaxation behavior.

Preparation of Interpolymers F, G, H, I, & J
Reactor Description

The single reactor used was a 6 gallon (22.7 L), oil jacketed, Autoclave continuously stirred tank reactor (CSTR). A magnetically coupled agitator with Lightning A-320 impellers provides the mixing. The reactor ran liquid full at 475 psig (3,275 kPa). Process flow was in the bottom and out the top. A heat transfer oil was circulated through the jacket of the reactor to remove some of the heat of reaction. After the exit from the reactor was a micromotion flow meter that measured flow and solution density. All lines on the exit of the reactor were traced with 50 psi (344.7 kPa) steam and insulated.

Procedure

Solvent, ethylbenzene unless stated, was supplied to the mini-plant at 30 psig (207 kPa). The feed to the reactor was measured by a Micro-Motion mass flow meter. A variable speed diaphragm pump controlled the feed rate. At the discharge of the solvent pump a side stream was taken to provide flush flows for the catalyst injection line (1 lb/hr (0.45 kg/hr)) and the reactor agitator (0.75 lb/hr (0.34 kg/ hr)). These flows were measured by differential pressure flow meters and controlled by manual adjustment of micro-flow needle valves. Uninhibited styrene monomer was supplied to the mini-plant at 30 psig (207 kpa). The feed to the reactor was measured by a Micro-Motion mass flow meter. A variable speed diaphragm pump controlled the feed rate. The styrene stream was mixed with the remaining solvent stream. Ethylene was supplied to the mini-plant at 600 psig (4,137 kPa). The ethylene stream was measured by a Micro-Motion mass flow meter just prior to the Research valve controlling flow. A Brooks flow meter/controllers was used to deliver hydrogen into the ethylene stream at the outlet of the ethylene control valve. The ethylene/hydrogen mixture combines with the solvent/styrene stream at ambient temperature. The temperature of the solvent/monomer as it enters the reactor was dropped to ~5 °C by an exchanger with -5°C glycol on the jacket. This stream entered the bottom of the reactor. The three component catalyst system and its solvent flush also enter the reactor at the bottom but through a different port than the monomer stream. Preparation of the catalyst components (catalyst; mixed alkyl aluminoxane(M-MAO); methyl dialkyl ammonium salt of tetrakis pentafluoroaryl borate) took place in an inert atmosphere glove box. The diluted components were put in nitrogen padded cylinders and charged to the catalyst run tanks in the process area. From these run tanks the catalyst was pressured up with piston pumps

and the flow was measured with Micro-Motion mass flow meters. These streams combine with each other and the catalyst flush solvent just prior to entry through a single injection line into the reactor.

Polymerization was stopped with the addition of catalyst kill
5 (water mixed with solvent) into the reactor product line after the micromotion flow meter measuring the solution density. Other polymer additives can be added with the catalyst kill. A static mixer in the line provided dispersion of the catalyst kill and additives in the reactor effluent stream. This stream next entered post reactor
10 heaters that provide additional energy for the solvent removal flash. This flash occurred as the effluent exited the post reactor heater and the pressure was dropped from 475 psig (3,275 kPa) down to ~250mm of pressure absolute at the reactor pressure control valve. This flashed polymer entered a hot oil jacketed devolatilizer. Approximately 85
15 percent of the volatiles were removed from the polymer in the devolatilizer. The volatiles exit the top of the devolatilizer. The stream was condensed and with a glycol jacketed exchanger, entered the suction of a vacuum pump and was discharged to a glycol jacket solvent and styrene/ethylene separation vessel. Solvent and styrene were
20 removed from the bottom of the vessel and ethylene from the top. The ethylene stream was measured with a Micro-Motion mass flow meter and analyzed for composition. The measurement of vented ethylene plus a calculation of the dissolved gasses in the solvent/styrene stream were used to calculate the ethylene conversion. The polymer separated in
25 the devolatilizer was pumped out with a gear pump to a ZSK-30 devolatilizing vacuum extruder. The dry polymer exits the extruder as a single strand. This strand was cooled as it was pulled through a water bath. The excess water was blown from the strand with air and the strand was chopped into pellets with a strand chopper.

Table 5

	Reactor Temp. °C	Solv. Flow		Ethylene Flow		Hydro- gen Flow		Styrene Flow		Vent Conv. %
		lb/hr	kg/hr	lb/hr	kg/hr	SCCM	lb/hr	kg/hr	lb/hr	
INTER POLYM ER										
F ⁽¹⁾ *	970226-1300	61.4	19.2	8.72	1.0	0.45	5.0		20.0	9.08
G ⁽ⁿ⁾	960922-1400	80.2	18.6	8.44	1.7	0.77	12.0		12.0	5.45
H ⁽ⁿ⁾	960924-0400	85.5	28.3	12.85	2.5	1.13	17.0		10.5	4.77
I ^(z)	961122-0600	83.7	28.5	12.94	2.1	0.95	7.0		9.8	4.45
J ⁽ⁿ⁾	961119-1600	108.9	26.6	12.07	3.0	1.36	5.0		9.0	4.09
										89.9

(1) Catalyst: C₉H₃-3-Ph-5,6-C₃H₆-SiMe₂-N(tBu)-TiMe₂(2) Catalyst: [(h₅-C₅Me₄)Me₂SiN(tBu)] Ti(CH₂=CH=CHMe)

- * This run was made with toluene solvent instead of ethylbenzene.

Examples 9-24

A summary of the blend components and blend compositions were given in Table 6.

Table 6

Blend Components	wt% S (ES)	Tg1, °C	Tg2, °C	Tm, °C/ Xty1	TMA, °C	Shore A	Flex Mod, MPa	Elong, %	Ult Ten, MPa	Eb, Nm	Stress Relax, %
F'	72.7	31.3	n/a	63	97	125.8	298	15	78.7		92.4
G'	57.5	3.7	n/a	57	64	5	1018	1.8	53.3		69
H'	52	-3.9	n/a	52	61	4	1218	2	34.7		80.1
I'	35.3	-5.3	63.8/13.3	78	86	29.7	566	23.3	139.9		32.5
J'	20.9	broad	90.3/28.5	99	91	80.9	647	30.4	197.4		30.8
Example No. : Blend Components (1/2/3)	Composition ratio (wt%)										
9: F/G	50/50	30.8	2.6	n/a	60	91	41.3	357	16.2	75.8	87.1
10: F/H	50/50	28.8	-7.5	n/a	58	91	34.9	360	14.1	71.3	88.9
11: F/G/H	33/33/34	30	1.6	n/a	55	80	26.3	549	7.1	53.9	86.3
12: I/G	25/75	2.8	s	65.8/10.0	58	69	14.1	768	5.5	47.1	68.1
13: I/G	50/50	3	s	66.6/10.6	68	77	20.9	627	14.8	93.3	52.5
14: I/G	75/25	1.9	s	65.7/16.3	76	80	20.3	622	23.9	147.4	43.3
15: I/F	25/75	31.7	-10.3	67.2/5.8	65	98	98.6	348	17.8	105.2	89.8
16: I/F	50/50	31.3	-8.8	65.9/6.2	73	97	58.6	436	21.7	13.3	77.4
17: I/F	75/25	33.1	-4.4	66.6/6.6	76	88	38	540	26.4	164.1	65.8
18: J/G	25/75	4.5	s	90.9/27.0	58	73	16.3	822	4.7	57.5	71.4
19: J/G	50/50	3.2	s	90.4/26.8	86	84	23.5	628	13.2	99.9	55.6
20: J/G	75/25	1.2	s	90.2/27.2	97	89	56.6	628	22.6	174.3	36.9

Table 6 cont'd

21: J/E	25/75	31.3	S	89.9/21.1	69	95	28.4	338	16.8	103.2	87.3
22: J/E	50/50	29.7	S	90.7/22.0	86	93	42.5	408	19.1	128	77.2
23: J/F	75/25	27.7	S	90.8/22.0	98	95	52.2	595	27.7	213.4	58.3
24: J/H/E	33/33/34	28.8	-5.9	89.4/22.1	71	90	20.8	412	12.3	82.4	80.9

* Not examples of the present invention.

Tg: measured from dynamic mechanical spectroscopy(DMS); maximum in tan δ loss peak for Tg.

Xtyl:

s: crystallinity; normalized with respect to blend composition.

s: shoulder or broad peak for Tg in DMS loss spectrum.

n/a:

not applicable.

Interpolymer F is an ethylene/styrene interpolymer which contains 41.8 mole (72.7 wt.) percent copolymerized styrene in the interpolymer, 9.1 wt. percent of atactic polystyrene and has an I_2 melt index of 2.5, and a melt index ratio I_{10}/I_2 of 10.1

5 Interpolymer G is an ethylene/styrene interpolymer which contains 26.7 mole (57.5 wt.) percent copolymerized styrene in the interpolymer, 3.5 wt. percent of atactic polystyrene and has an I_2 melt index of 1.0, and a melt index ratio I_{10}/I_2 of 7.6

10 Interpolymer H is an ethylene/styrene interpolymer which contains 22.6 mole (52 wt.) percent copolymerized styrene in the interpolymer, 1.8 wt. percent of atactic polystyrene and has an I_2 melt index of 1.0, and a melt index ratio I_{10}/I_2 of 7.4

15 Interpolymer I is an ethylene/styrene interpolymer which contains 12.8 mole (35.3 wt.) percent copolymerized styrene in the interpolymer, 8.6 wt. percent of atactic polystyrene and has an I_2 melt index of 1.1, and a melt index ratio I_{10}/I_2 of 7.6

20 Interpolymer J is an ethylene/styrene interpolymer which contains 6.6 mole (20.9 wt.) percent copolymerized styrene in the interpolymer, 7.7 wt. percent of atactic polystyrene and has an I_2 melt index of 1.0, and a melt index ratio I_{10}/I_2 of 8.0

The blend examples of Table 6 further illustrate the utility and unique property balances which can be achieved by blending of Interpolymers.

25 Blends 9, 10 show two distinct glass transition processes from dynamic mechanical testing, combined with high tensile energy at break and a level of stress relaxation biased towards the performance of component (E).

30 Blend 11 shows two distinct glass transition processes from dynamic mechanical testing, reflecting the miscibility of components G and H giving a single T_g peak, with component F being present as a separate phase. This blend retains good mechanical properties and high stress relaxation.

35 Blends 12-17 show either a broad temperature range for T_g , or two distinct T_g processes, combined with high tensile energies at break and unexpected levels of stress relaxation compared to what may be anticipated from the component polymers.

40 Blends 18-23 further illustrate that good thermal performance, as evidenced by TMA probe penetration, can be achieved whilst retaining good mechanical properties and high stress relaxation behavior.

CLAIMS:

- 1 1. A blend of polymeric materials characterized by a
2 plurality of interpolymers, each interpolymer resulting from
3 polymerizing:
 - 4 (1) from 1 to 65 mole percent of either
 - 5 (a) at least one vinylidene aromatic monomer or
 - 6 (b) at least one hindered aliphatic or cycloaliphatic vinylidene
7 monomer, or
 - 8 (c) a combination of at least one vinylidene aromatic monomer
9 and at least one hindered aliphatic or cycloaliphatic
10 vinylidene monomer, and
 - 11 (2) from 35 to 99 mole percent of at least one aliphatic alpha olefin
12 having from 2 to 20 carbon atoms; and
 - 13 (3) from 0 to 10 mole percent of at least one polymerizable olefin
14 monomer different from (2); and
- 15 wherein:
 - 16 (i) the amount of vinylidene aromatic monomer residue and/or
17 hindered aliphatic or cycloaliphatic vinylidene monomer residue
18 in any interpolymer differs from that amount in any other
19 interpolymer) by at least 0.5 mole percent; and/or
 - 20 (ii) there is a difference of at least 20 percent between the number
21 average molecular weight (M_n) of each interpolymer component.
- 1 2. A blend of claim 1, wherein each of the interpolymer
2 components result from polymerizing:
 - 3 (1) from 1 to 65 mole percent of either
 - 4 (a) at least one vinylidene aromatic monomer or
 - 5 (b) at least one hindered aliphatic or cycloaliphatic vinylidene
6 monomer, or
 - 7 (c) a combination of at least one vinylidene aromatic monomer
8 and at least one hindered aliphatic or cycloaliphatic
9 vinylidene monomer, and
 - 10 (2) from 35 to 99 mole percent of at least one aliphatic alpha olefin
11 having from 2 to 12 carbon atoms; and
 - 12 (3) from 0 to 10 mole percent of at least one polymerizable olefin
13 monomer different from (2); and
- 14 wherein:
 - 15 (i) the amount of vinylidene aromatic monomer residue and/or
16 hindered aliphatic or cycloaliphatic vinylidene monomer residue
17 in any interpolymer component differs from that amount in
18 another interpolymer component by at least 1 mole percent;
19 and/or

20 (ii) there is a difference of at least 30 percent between the number
21 average molecular weight (Mn) of each interpolymer component.

1 3. A blend of claim 1, wherein each of the interpolymer
2 components result from polymerizing a composition comprising:

- 3 (1) from 1 to 65 mole percent of styrene and
4 (2) from 35 to 99 mole percent of ethylene or a combination of
5 ethylene and at least one higher aliphatic alpha olefin having
6 from 3 to 12 carbon atoms; and

7 wherein:

- 8 (i) the amount of styrene residue in any interpolymer component
9 differs from that of another interpolymer component by at least
10 .2 mole percent; and/or
11 (ii) there is a difference of at least 40 percent between the number
12 average molecular weight (Mn) of each interpolymer component.

1 4. A blend of claim 1, wherein each of the interpolymer
2 components results from polymerizing:

- 3 (1) from 1 to 65 mole percent of styrene and
4 (2) from 35 to 99 mole percent of ethylene or a combination of
5 ethylene and at least one of propylene, 4-methyl pentene,
6 butene-1, hexene-1, octene-1 or norbornene

7 wherein:

- 8 (i) the amount of styrene residue in any interpolymer component
9 differs from that amount in another interpolymer component by
10 at least 0.5 mole percent; and/or
11 (ii) there is a difference of at least 20 percent between the number
12 average molecular weight (Mn) of each interpolymer component.

1 5. A blend of claim 1, wherein each of the interpolymer
2 components results from polymerizing:

- 3 (1) from 1 to 65 mole percent of styrene and
4 (2) from 35 to 99 mole percent of ethylene; or a combination of
5 ethylene and at least one of propylene, 4-methyl pentene,
6 butene-1, hexene-1, octene-1 or norbornene

7 wherein:

- 8 (i) the amount of styrene residue in any interpolymer component
9 differs from that in another interpolymer component by at least
10 1 mole percent; and/or
11 (ii) there is a difference of at least 30 percent between the number
12 average molecular weight (Mn) of interpolymer components.

1 6. A blend of claim 1, wherein each of the interpolymer
2 components results from polymerizing:

- 3 (1) from 1 to 65 mole percent of styrene and
4 (2) from 35 to 99 mole percent of ethylene or a combination of
5 ethylene and at least one of propylene, 4-methyl pentene,
6 butene-1, hexene-1,octene-1 or norbornene; and

7 wherein:

8 the amount of styrene residue in any interpolymer component differs
9 from that amount in another interpolymer component by from 2 to less
10 than 10 wt. percent, such blends exhibiting a single glass
11 transition temperature (Tg) similar in form to, but in the
12 temperature range between the Tg's of the individual interpolymer
13 components as measured by dynamic mechanical spectroscopy.

1 7. A blend of claim 1, wherein each of the interpolymer
2 components results from polymerizing:

- 3 (1) from 1 to 65 mole percent of styrene and
4 (2) from 35 to 99 mole percent of ethylene or a combination of
5 ethylene and at least one of propylene, 4-methyl pentene,
6 butene-1,
7 hexene-1, octene-1 or norbornene wherein:

8 the amount of styrene residue in any interpolymer component differs
9 from that amount in another interpolymer component by greater than
10 10 wt.%, such blend compositions exhibiting a broadened single glass
11 transition temperature range, or exhibiting two or more glass
12 transition temperatures as measured by dynamic mechanical
13 spectroscopy.

1 8. A blend of claim 1, comprising three or more
2 interpolymer components resulting from polymerizing:

- 3 (1) from 1 to 65 mole percent of styrene and
4 (2) from 35 to 99 mole percent of ethylene or a combination of
5 ethylene and at least one of propylene, 4-methyl pentene,
6 butene-1, hexene-1,octene-1 or norbornene wherein:

7 wherein the overall blend composition exhibits a broadened single
8 glass transition temperature range, or exhibits two or more distinct
9 glass transition temperatures as measured by dynamic mechanical
10 spectroscopy.

1 9. A blend of any of claims 1-8 wherein the interpolymer
2 components are produced by copolymerization of two or more appropriate
3 monomers in the presence of a metallocene catalyst and a co-catalyst.

1 10. An adhesive or sealant system comprising an
2 interpolymer blend of any one of claims 1-9.

1 11. Sheet or film resulting from calendering, blowing or
2 casting an interpolymer blend of any one of claims 1-9.

1 12. Injection, compression, extruded, blow molded,
2 rotomolded or thermoformed parts prepared from an interpolymer blend
3 of any one of claims 1-9.

1 13. Fibers, foams or latices prepared from an
2 interpolymer blend of any one of claims 1-9.

1 14. Fabricated articles, or foamed structures prepared
2 from an interpolymer blend of any one of claims 1-9 and finding
3 utility in sound and vibration damping applications.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/15546

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08L25/02 C08L23/02

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 27755 A (DOW CHEMICAL CO) 19 October 1995 cited in the application see claims ---	1
A	WO 95 32095 A (GRACE W R & CO ;BRADFUTE JOHN G (US); CHILDRESS BLAINE C (US); HAV) 30 November 1995 cited in the application see page 19, line 7 - page 20, line 13; claims ---	1
A	EP 0 416 815 A (DOW CHEMICAL CO) 13 March 1991 cited in the application see page 13, line 1 - line 14; claims -----	1

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/15546

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO 9527755 A	19-10-95	US 5460818 A		24-10-95
		AU 2281195 A		30-10-95
		CA 2187640 A		19-10-95
		CN 1146211 A		26-03-97
		EP 0755418 A		29-01-97
		FI 964099 A		11-10-96
-----	-----	-----	-----	-----
WO 9532095 A	30-11-95	US 5658625 A		19-08-97
		AU 2639795 A		18-12-95
		CA 2191090 A		30-11-95
		EP 0765219 A		02-04-97
-----	-----	-----	-----	-----
EP 0416815 A	13-03-91	AT 156827 T		15-08-97
		AU 645519 B		20-01-94
		AU 6203990 A		07-03-91
		CA 2024333 A		01-03-91
		DE 69031255 D		18-09-97
		EP 0764653 A		26-03-97
		EP 0764664 A		26-03-97
		EP 0764654 A		26-03-97
		EP 0774468 A		21-05-97
		EP 0765888 A		02-04-97
		HU 209316 B		28-04-94
		JP 7053618 A		28-02-95
		JP 2623070 B		25-06-97
		JP 7070223 A		14-03-95
		JP 2535249 B		18-09-96
		JP 3163088 A		15-07-91
		NO 176964 B		20-03-95
		NO 179043 B		15-04-96
		NO 301376 B		20-10-97
		NO 954469 A		01-03-91
		RU 2073018 C		10-02-97
		CN 1049849 A, B		13-03-91
		PL 166689 B		30-06-95
-----	-----	-----	-----	-----

